# Guided random walk calculation of energies and $\langle \sqrt{r^2} \rangle$ values of the $^1\Sigma_g$ state of $H_2$ in a magnetic field.

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## Abstract

Energies and spatial observables for the  ${}^{1}\Sigma_{g}$  state of the hydrogen molecule in magnetic fields parallel to the proton-proton axis are calculated with a guided random walk Feynman-Kac algorithm. We demonstrate that the accuracy of the results and simplicity of the method may prove it a viable alternative to large basis set expansions for small molecules in applied fields.

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## 1.Introduction

The physics of the  $H_2$  molecule in magnetic fields is a problem of interest in molecular physics [1,2], astrophysics [3], and to some extent in condensed matter physics [4]. A series of papers examining  $H_2$  in magnetic fields parallel to the proton-proton axis have recently been published [5,6]. These papers use basis set expansions to compute potential energy curves and equilibrium values of the proton-proton radial separation for several of the low lying states of the molecule. While this program has been successful, it is useful to have alternate methods that have their own advantages. Work has been done on this problem with a fixed phase Monte Carlo algorithm [7] that is general and may prove to be the eventual method of choice for other molecules in magnetic fields. Here however we have chosen a guided random walk Feynman-Kac (GRWFK) algorithm [8,9,10] because of it's ease of implementation and extension to other molecular systems. GRWFK also has the advantage of avoiding trial wavefunction contamination of quantities calculated with the method.

This brief report is organized as follows: In section 2 we give an outline of the calcu-

lational method. In section 3 we apply the method to the  ${}^{1}\Sigma_{g}$  state of  $H_{2}$  in a magnetic field. Section 4 presents results for the energies and electronic  $\langle \sqrt{r^{2}} \rangle$  values of the molecule for some representative fields. Section 5 is reserved for conclusions.

## 2. Calculational method

We give a brief discussion of the calculational method for one dimensional systems. The extension to higher dimensionality is very simple and is an advantage of the formalism.

The Feynman-Kac formula [11,12] for a walker starting a walk at x', T' = 0, 0 is

$$U(x, T, x' = 0, T' = 0) = \langle exp \left[ - \int_{0}^{T} ds \ V(B(s) + x) \right] \rangle = \sum_{n} \Psi_{n}(x) \Psi_{n}(0) e^{-E_{n}T}.$$
 (1)

U(x, T, 0, 0) is the Euclidian quantum mechanical propagator and the brackets denote an expectation value over the Weiner measure [13]. The argument of the exponential is an integral of the potential along a Gaussian process of mean zero and variance one [14] (we choose this as a Bernoulli sequence of plus and minus ones). Computationally this amounts to evaluating

$$U_{one\ path}(x, T, x' = 0, T' = 0) \approx exp[-\frac{1}{n} \sum_{k=0}^{nT} V(\frac{B_k}{\sqrt{n}} + x)]$$
 (2)

a large number N times. In practice the energy is better approximated by

$$E_0 \approx \frac{1}{T_2 - T_1} \ln \left[ \frac{U(T_2)}{U(T_1)} \right] \tag{3}$$

with  $T_1, T_2$ , two sufficiently large times.

It is known the F-K formula as written in eq.(1) and it's discretized form in eq.(2) are formally correct but plagued by slow convergence and large variance when employed for numerical work. There are many schemes in the literature that address this problem. Here we adopt a method that has the advantage of simplicity and adaptability to parallelization.

An unconstrained random walk has equal probability  $P = \frac{1}{2}$  to step left or right. The probability distribution  $\rho(x, \tau + \Delta \tau)$  for the arrival of a walker at  $x, \tau$  is

$$\rho(x, \tau + \Delta \tau) = \frac{1}{2}\rho(x - \Delta x, \tau) + \frac{1}{2}\rho(x + \Delta x, \tau).$$

This leads to

$$-\frac{\partial \rho}{\partial \tau} = -\frac{1}{2} \frac{h_x^2}{h_\tau} \frac{\partial^2 \rho}{\partial^2 x}.$$
 (4)

If instead the walk probabilities for a step right or left are modified by a guiding function g(x) such that

$$P_{L,R} = \frac{1}{2} \pm \frac{\partial g}{\partial x} \tag{5}$$

then in the continuum limit with  $\frac{h_x^2}{h_\tau} \to 1$  a modified diffusion equation (inclusion of the potential V is simple [8]) for the probability distribution becomes

$$-\frac{\partial \rho}{\partial \tau} = -\frac{1}{2} \frac{\partial^2 \rho}{\partial^2 x} - 2 \frac{\partial g}{\partial x} \frac{\partial \rho}{\partial x} + \rho \frac{\partial^2 g}{\partial^2 x} + V \rho. \tag{6}$$

Although formally  $\rho$  ought to be replaced with another symbol to account for inclusion of V(x) it should cause no confusion here.

By setting  $\rho = e^{-2g}U$  eq.(6) becomes

$$-\frac{\partial U}{\partial \tau} = -\frac{1}{2} \frac{\partial^2 U}{\partial^2 x} + \Omega U,\tag{7}$$

$$\Omega(x) = V(x) - 2\left[\frac{\partial g(x)}{\partial x}\right]^2 + \frac{\partial^2 g(x)}{\partial^2 x}.$$
 (8)

Since  $g = -\frac{1}{2}lnU$  (from  $\rho \propto \Psi^2$ ) knowledge of the solution of eq.(6) give would the exact guiding function g(x) and vice-versa. Of course U is not generally known, but by choosing g(x) to incorporate what is known about the general character of the solution the variance of calculated observables can be reduced and convergence to the final result can be substantially improved. In what follows we evaluate eq.(7) with conditional probabilities given by eq.(5), and use  $\Omega(x)$  rather than V(x) as the argument of the exponential in eq.(2). For the ground state  $U \propto \Psi_0$  so we refer to trial wavefunctions rather than propagators below.

The ground state expectation value of an operator  $O(\mathbf{r}_1)$  can be found by evaluating

$$\langle O \rangle = \frac{\sum_{\mathbf{r}_1} O(\mathbf{r}_1) |\Psi(\mathbf{r}_1)|^2}{\sum_{\mathbf{r}_1} \left|\Psi(\mathbf{r}_1)\right|^2}.$$

For large times  $T_1, T_2$  the rightmost term of eq. (1) can be used to generate  $|\Psi(\mathbf{r}_1)|^2$ , hence  $\langle O \rangle$ : Evolve the walk to to time  $T_1$ , tallying the value of the exponential of eq.(2) for each

path at  $T_1$ . Multipy this value by  $\langle O(T_1) \rangle$ , then evolve the walk to  $T_2$ . With

$$w_i = expig[-\int\limits_0^{T_2} d\mathbf{s}\Omega(\mathbf{s})ig]_i$$

this yields

$$\langle O \rangle = \frac{\sum_{i=1}^{N} w_i [O(T_1)]_i}{\sum_{i=1}^{N} w_i}.$$

It is worth noting that we do not generate random walks on a three dimensional grid for each particle but rather as three separate one dimensional grids. This is why the three dimensional spatial branching factor of 6 used by Barnes et.al. does not appear above.

## 3. Application to $H_2$ in a magnetic field.

In the clamped nuclei approximation the Hamiltonian of the  $H_2$  molecule in a magnetic field B may be written in natural units as

$$\sum_{i=1}^{2} \left[ -\frac{1}{2} \nabla^{2}_{i} - \frac{1}{\left| \mathbf{r}_{i} - \frac{\mathbf{R}}{2} \right|} - \frac{1}{\left| \mathbf{r}_{i} + \frac{\mathbf{R}}{2} \right|} + \frac{1}{8} \left[ \frac{\mathbf{B}}{B_{0}} \times \mathbf{r}_{i} \right]^{2} \right] + \frac{1}{2} \frac{\mathbf{B}}{B_{0}} \cdot \mathbf{L} + \frac{1}{\left| \mathbf{r}_{1} - \mathbf{r}_{2} \right|} + \mathbf{S} \cdot \frac{\mathbf{B}}{B_{0}} + \frac{1}{R}$$
(9)

with  $B_0 = 2.3505 \times 10^9 G$ . Taking B along the z axis reduces eq. (9) for the  $^1\Sigma_g$  state to

$$\sum_{i=1}^{2} \left[ -\frac{1}{2} \nabla^{2}_{i} - \frac{1}{\left| \mathbf{r}_{i} - \frac{\mathbf{R}}{2} \right|} - \frac{1}{\left| \mathbf{r}_{i} + \frac{\mathbf{R}}{2} \right|} + \frac{1}{8} \gamma^{2} \left( x_{i}^{2} + y_{i}^{2} \right) \right] + \frac{1}{\left| \mathbf{r}_{1} - \mathbf{r}_{2} \right|} + \frac{1}{R}, \quad (10)$$

$$\gamma = \frac{B}{B_{0}}.$$

For the trial  ${}^{1}\Sigma_{g}$  wavefunction it is convenient to first define the auxiliary quantities

$$f_i^{\pm} = -\left|\mathbf{r}_i \pm \frac{\mathbf{R}}{2}\right|.$$

The trial wavefunction is then

$$\Psi_t(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) = \left[ e^{f_1^+} + e^{f_1^-} \right] \left[ e^{-\frac{\gamma}{4}(x_1^2 + y_1^2)} \right] \times \left[ 1 \to 2 \right]$$
(11)

It is straightforward to insert the  $\Psi_t$  of eq. (11) into the expression for g to obtain  $\Omega$  and the modified walk probabilities. We note in passing that this choice amounts to a

baseline level trial function. No a priori attempt was made to include free parameters for later optimization.

## 4. Results

In table 1 we give  $E_0$  in atomic units for several values of  $\gamma$  at the indicated  $R_{eq}$ . We also give  $E_0$  for  $\gamma = 2.127207$  at  $R_{eq} = 1.07$  a.u. There are two values in the literature for  $E_0$  at this field strength [6,15]. Our value confirms the result of Detmer et. al. in [6].

These results show good agreement with [6] for the relatively small number of sample paths considered here. The value n=800 was arrived at by starting at n=200 and increasing n by 100 steps per run for a few thousand sample paths. n=500 was found to be sufficient for all  $\gamma$  considered. 300 more steps were added as a check on the stability of convergence. We give the results for the larger n. A similar method was employed for the determination of  $T_1$  and  $T_2$ . (We did not include disassociation values since they were also the same as those given in [6].) In table 2 we show results for calculations of  $\langle \sqrt{r^2} \rangle$  for some values of  $\gamma$ . We were interested in the value of the field for which the rms value equaled the proton's separation believing this to be a reasonable albeit naive measure of the onset of the transition to the free atomic limit. Clearly the field value at which this would occur is large enough to align the spins making the triplet rather than the singlet state the correct state to investigate. It should be noted that the times  $T_1$  and  $T_2$  that give convergence of  $E_0$  usually were not sufficient to converge  $\langle \sqrt{r^2} \rangle$ . This is reflected in the larger values of  $T_1$  and  $T_2$  in table 2.

#### 5. Conclusions

The accuracy of the GRWFK method for this problem suggests that faster convergence with basis set expansions might be achieved with LCAO trial wavefunctions functions multiplied by oscillator eigenstates. This is a direction best explored by those working already with that method. Certainly basis sets expansions prove (at least for fixed nuclei) a superior method for digit aquisition than Monte Carlo methods. The trade off between accuracy and ease of implementaion for molecules like  $H_3$  or even  $H_3^+$  in a magnetic field is an open question.

Calculating the properties of low-lying excited states is not unfeasable but is known

to be limited by the (lack of) knowledge of the nodal structure of the state [16,17]. The fixed node method [18,19] has been shown as a good approximation for small molecular systems [20]. For biased random walks the nodal structure can be built into the trial functions although not without increased complexity. Clearly states of non-zero orbital angular momentum will have to be considered by incorporating the techniques discussed in [7] to GRWFK. This is a topic of current investigation.

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Table 1  $^{1}\Sigma_{g}$  state energies as functions of magnetic field B and  $R_{eq}$ . All units are in a.u. Bracketed numbers are last digit uncertainty estimates from variance calculations for N=50000 sample paths.  $n=800, T_{1}=7, T_{2}=8$  for all entries.

		Ref. [6]	This work
$\gamma$	$R_{eq}$	$E_0$	$E_0$
.01	1.40	-1.173436	-1.172(2)
.10	1.39	-1.169652	-1.169(1)
1.0	1.24	-0.890336	-0.889(1)
10.0	.70	5.88902	5.888(3)

Table 2  $^{1}\Sigma_{g}$   $\sqrt{r^{2}}$  values in a.u.for some values of B. Data below are for  $n=800, T_{1}=10, T_{2}=12$  and N=50000 sample paths. Larger times are needed to converge  $\sqrt{r^{2}}$  compared to those needed for  $E_{0}$ . The last entry in the table serves as a check on the dissacociative limit.

$\gamma$	$R_{eq}$	$\sqrt{r^2}$
.01	1.40	1.565(3)
1.0	1.24	1.326(2)
2.0	1.09	1.141(3)
5.0	0.86	0.882(2)
7.5	0.74	0.782(1)
10.0	0.70	0.658(2)
0.0	50.0	1.495(2)